



Laboratory Study of Volatile Organic Compound Partitioning

Vapor/Aqueous/Soil

Alan D. Hewitt

February 1998

Abstract: A laboratory experiment measured the concentrations of volatile organic compounds (VOCs) existing in a vapor, water, and bulk soil media after several weeks of exposure to a contaminant source. The experimental design included quiescent conditions, hydrated mineral surfaces, and a constant tem-

perature of $11 \pm 1^\circ\text{C}$. The findings show that similar to Henry's law, fairly constant ratios are likely to exist between soil vapor and bulk soil VOC concentrations. These results are encouraging for those attempting to use active soil gas measurements to predict bulk VOC concentrations in the vadose zone.

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PREFACE

This report was prepared by Alan D. Hewitt, Research Physical Scientist, Geological Sciences Division, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL).

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This publication reflects the view of the author and does not suggest or reflect policy, practices, programs, or doctrine of the U.S. Army or of the Government of the United States.

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INTRODUCTION

Unlike the other two major classes of hazardous waste constituents, semivolatile organic compounds and metals, volatile organic compounds (VOCs) have high vapor pressures that allow substantial portions of these analytes to exist in a gaseous state under most environmental conditions. As a result, often a contaminant vapor plume accompanies the infiltration of VOCs as a residual product through the vadose zone or as a solute in groundwater (within the saturated zone or in percolating rainwater). Moreover, the diffusive and advective properties of gases make this mode of subsurface transport one of the most rapid and pervasive (Conant et al. 1996). Because of these properties, active soil vapor analysis (which is a relatively inexpensive, rapid, and nonintrusive method of sample collection and analysis) has seen increasingly greater use as a means of characterizing VOC contamination at suspected hazardous waste sites. However, this approach is only qualitative with respect to the concentrations present in the bulk material on a mass per mass basis. That is, no simple relationship exists between the empirically established concentrations for soil vapor and soil mass concentrations.

When attempts have been made to use experimentally developed equilibrium models to predict environmental VOC concentrations between vapor and the bulk soil matrix, discrepancies of more than one order of magnitude have resulted between theoretical and measured values (Smith et al. 1990, Cho et al. 1993). Similarly, most studies dealing solely with environmental samples have

failed to demonstrate significant correlations between VOC concentrations in soil vapor and collocated bulk or discrete soil samples (Sextro 1996, Minnich et al. 1997). A possible explanation for these discrepancies involves the experimental design and implementation of both laboratory and field studies. Laboratory experiments traditionally have used relatively short (<1- to 2-day) equilibrium periods and have often failed to include soil moisture levels representative of field conditions (Smith et al. 1990, Unger et al. 1996). The major problem for most field studies is the use of inadequate sampling procedures. For example, current soil sampling and handling methods used for VOC characterization are likely to grossly underestimate their concentrations because of losses from volatilization and biodegradation between the time of collection and analysis (Hewitt et al. 1995, Liikala et al. 1996).

Modeling the vapor-phase transport and sorption characteristics of VOCs in soil has been the topic of numerous publications (Pignatello and Xing 1996). The vast majority of the studies dealing with these two topics has depended solely on laboratory experiments. A notable exception was a recent field study of Conant et al. (1996), where the transport of trichloroethene in the unsaturated zone was empirically and theoretically modeled. This study demonstrated that the vapor plume originating from a residual product source could rapidly spread throughout the adjoining unsaturated zone, contaminating (among other features) the capillary fringe and subsequently the underlying saturated zone.

When developing a theoretical model to

describe the transport of gaseous TCE, Conant et al. (1996) used linear partitioning to characterize the interactions with the bulk soil matrix. This model considered only solid–aqueous phase partitioning, omitting solid–vapor phase partitioning. Implicit to the omission of solid–vapor partitioning is that all mineral surfaces were considered to be hydrated, a condition that prevails in humid and temperate climates. Hydrated mineral surfaces usually exist when the bulk soil has a moisture content of a percent or more. Therefore, the model assumes that the distribution of VOCs between the vapor phase and bulk soil can be described by a proportionality constant, analogous to the Henry's law constant, i.e., the ratio between vapor and aqueous VOC concentrations under equilibrium conditions. With regard to the sorption capacity of the bulk soil matrix for VOCs, Conant et al.'s model considered the organic carbon content to be the dominant variable, with soil moisture content playing a smaller role.

This study describes a laboratory approach for assessing vapor–water and vapor–soil partitioning of VOCs under conditions typical of the subsurface in temperate climates. Notable differences from most previous studies are the use of exposure periods of three or more weeks, quiescent conditions, hydrated mineral surfaces, and a constant temperature of $11 \pm 1^\circ\text{C}$. The intent of these experiments was not to assess the transport characteristics of VOCs, but to estimate the quasi-equilibrium concentration relationships that are likely to exist among vapor, water, and soil grab samples.

OBJECTIVE

The objective of this study is to better understand the concentrations of VOCs that exist among the vapor, water, and bulk soil media. To achieve this goal, VOCs were passively transferred by a vapor fortification process (Hewitt and Grant 1995) to these three different media, held at $11 \pm 1^\circ\text{C}$ in a vapor-tight chamber. Furthermore, relatively long exposure periods (>21 days) were used in an attempt to create a quasi-equilibrium condition for vapor–bulk soil partitioning. The equilibria are only considered to be quasi, because VOC sorption has been assumed to follow a similar biphasic process as desorption (Steinberg et al. 1987). Therefore, soils most likely continue to sorb VOCs over a very long time (on the order of months to years) because of diffusion-limited processes occurring within the soil matrix.

EXPERIMENTAL

Apparatus and materials

The chambers used for these studies consisted of 500-mL glass jars capped with a Teflon-backed silicone septum cap (I-Chem), which allows for syringe-needle penetration. The vessels used for discrete soil and liquid samples were clear glass 2.00-mL autosampler vials with open top screw caps and PTFE-faced silicone septa (Supeloc, Inc). These small vials were modified to allow for the exchange of VOC vapors between the discrete sample and the chamber atmosphere, while limiting the transfer of water vapor. Gaskets were made out of the septa by punching a 3-mm-diam. holes out of the center of each. Hydrophobic membranes 7.5 mm in diameter were then punched out of a 20- × 20-cm sheet (\approx 4-mil) of Durapel (Millipore). When in use, these hydrophobic membranes were placed below the septa (PTFE face adjacent to membrane). In this arrangement the Durapel membrane disk is pressed between the rim of the glass vial and the Teflon-faced septum gasket (Fig. 1).

The chamber also contained two 20-mL glass bottles, one of which contained a vapor fortification solution and the other contained 10 mL of

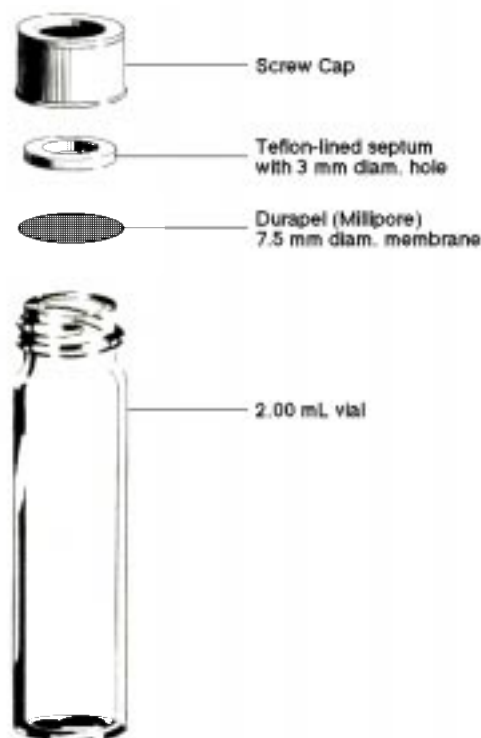


Figure 1. Modified vial used for holding soil and water samples in the exposure chamber.

groundwater. The vapor fortification solutions were prepared by adding small volumes (0.1 μL to 0.5 mL) of six different VOCs to 2.0 mL or more of reagent-grade tetraethylene glycol dimethyl ether (tetraglyme). The VOCs chosen for this study, trans-1,2-dichloroethene (TDCE), trichloroethene (TCE), tetrachloroethene (PCE), benzene (Ben), toluene (Tol), para-xylene (p-Xyl), were also reagent grade. The second 20-mL bottle containing 10 mL of groundwater served as a source of moisture to the chamber.

Three soils were used, a silty/sand (CR-S), a sandy/silt (CR-D), and a coarse sand from Wisconsin (Wis). The first two soils were collected at the Cold Regions Research and Engineering Laboratory (CRREL) and the Wis soil from Shawano County, Wisconsin. The CR-S soil was obtained from the topsoil (10–30 cm), and the CR-D soil, from depths greater than 30 m below the surface, and the Wis soil was a clean sand taken from a depth of 60 cm. All three soils were air dried, passed through a 30-mesh sieve, and thoroughly mixed. Portions of these air-dried soils (<1% moisture, ASTM D2216-66) were transferred to plastic bottles and wetted by adding a locally obtained groundwater, creating four moisture conditions for each. The moisture contents at the beginning of the exposure period, general soil classifications, and organic carbon contents are listed in Table 1.

Table 1. Soil moisture levels, general classification, and percentage of organic carbon.

	Air dried*	% Moisture (initial)				% Organic carbon**
		5%	10%	20%	Sat'd†	
CRREL surface (silty/sand-loam)	✓		✓	✓	✓	0.88
CRREL deep (sandy/silt)	✓		✓	✓	✓	0.10
Wisconsin (sand)	✓	✓	✓		✓	0.17

* <1% moisture

† Water saturated

** As determined by Leco CR-12 furnace analysis (Merry and Spouncer 1988).

Procedure

By using a funnel, spatula, and metal rod, portions of each of the three soil types at the preset moisture conditions (3 soil types \times 4 moisture contents) were transferred to the small (2-mL) pre-weighed sample vials. These vials were filled to capacity, leaving very little (0.1- to 0.3-mL) headspace, while creating fairly consistent and environmentally representative bulk soil densities (Ta-

Table 2. Bulk soil densities for various test samples.

	Air dried*	% Moisture (initial)			
		5%	10%	20%	Sat'd†
CRREL surface (silty/sand-loam)	1.24** ± 0.06		1.46 ± 0.04	1.57 ± 0.04	1.76 ± 0.09
CRREL deep (sandy/silt)	1.62 ± 0.05		1.64 ± 0.06	1.89 ± 0.04	2.06 ± 0.07
Wisconsin (sand)	1.56 ± 0.04	1.65 ± 0.03	1.72 ± 0.04		2.01 ± 0.03

* <1% moisture

† Water saturated

** Density (g/cm^3)

ble 2). After filling a vial with soil, the rim was wiped clean and the weight of the contents determined. Following this second weighing, the cap and hydrophobic membrane were secured onto the vial and a third weight was taken. In addition, two vials were half filled (1 mL) with groundwater, covered with the hydrophobic membrane, and weighed.

Once all the membrane-covered soil and water-containing vials had been placed into a chamber, a vapor fortification solution was prepared by adding neat VOCs to tetraglyme held in a 20-mL glass bottle. To prepare this organic cocktail solution with 0.1 μL of each the six VOCs (Table 3), a 1- μL microvolume syringe (SGE) was used. Neat analytes were added to the other cocktail solutions using 10-, 100-, and 500- μL syringes (Hamilton), respectively. The vapor fortification solution and a 20-mL glass bottle containing 10 mL of groundwater were the last two vessels added to the chamber. The bottle containing 10

Table 3. Samples, fortification solution composition, and exposure period for each chamber experiment.

Expt. no.	Equilibration period (days)	Single or duplicates	Volume (mL)	
			VOCs*	Tetraglyme
1	27	A	0.0001	5
2	22	B	0.001	5
3	22	A	0.01	5
4	24	B	0.1	4.5
5	25	B	0.5	2
6	50	B	0.01	5
7	49	B	0.1	5
8	55	B	0.001	5

A—Single sample of each soil type at four different moisture contents and two groundwater samples.

B—Duplicate samples of CRREL soils (except single sample for saturated condition) at various moisture contents, single replicate of Wisconsin soil at four moisture contents, and two groundwater samples.

* Volume of TDCE, Ben, TCE, Tol, PCE and P-Xyl added.

mL of water was included to serve as a source of moisture to the chamber atmosphere. Then the chambers were capped and allowed to stand for periods of 3 weeks or longer in an incubator held at $11 \pm 1^\circ\text{C}$. In all, eight chambers were prepared in this fashion. Table 3 lists the quantities and types of samples, length of exposure, and the contents of the organic vapor fortification solution used for each experiment.

At the end of the exposure period, the chamber was removed from the incubator and a 0.5-mL gastight syringe (Hamilton) was used to immediately remove a 500- μL headspace sample of the chamber gas. This sample, representative of the vapor concentration at the end of the exposure period, was immediately transferred to a sealed 22-mL autosampler volatile organic compound analysis (VOA) vial (Wheaton). Because of the limited volume of the analysis VOA vial, two needles of the same gauge (22 gauge) were used for this transfer step. The tip of a second needle, which served as a pressure vent, was positioned adjacent to the Teflon-lined septum (near the cap), while the needle used to transfer the sample of chamber gas was positioned in the middle of the VOA vial. Both needles were quickly removed after the transfer was completed (≈ 3 seconds). Three separate headspace sample replicates were prepared in this fashion, using two different syringes. This number of replicates and use of two syringes was necessary because the needles can become partially clogged with pieces of septa during the retrieval and transfer process.

After removing the vapor samples, the chamber was opened. For six of the eight experiments the glass bottle containing 10 mL of groundwater was sampled twice with a 1.00-mL pipette. These aliquots of water from the uncovered moisture reservoir were transferred directly to a 22-mL autosampler VOA vial containing 10 mL of Type 1 water. Similarly each of the 2-mL sample vials were transferred to a VOA vial containing 10 mL of water after weighing and removing the cap and membrane. Immediately, after transferring these samples, a Teflon-lined gray butyl rubber and aluminum crimp top was used to seal the headspace autosampler VOA vials. Special precautions were taken when transferring a sample vial to an autosampler VOA vial containing 10 mL of Type 1 water, so as not to disturb or spill, respectively, the contents of either vessel.

Analysis

On the same day the samples were removed

from the chamber, they were analyzed by headspace gas chromatography (HS/GC). The analysis system used consisted of a HS autosampler (Tekmar 7000), coupled to a GC (SRI, model 8610-0058) equipped with a 15-m DB-1 0.53-mm capillary column and photo and flame ionization sequential detectors. The settings used for both of these instruments have been reported elsewhere (Hewitt 1995a). One exception was for the analysis of the chamber vapor samples, where a platen temperature of 40°C was used. In preparation for analysis the water and soil samples were gently hand shaken until all of the vial contents had been completely dispersed.

Analyte concentrations were established relative to working standards prepared by transferring small ($<10 \mu\text{L}$) quantities from a methanol stock solution. Working standards prepared for the chamber gas samples were placed in empty autosampler VOA vials, while those for the soil and water samples were added to 10 mL of Type 1 water (Hewitt et al. 1992).

RESULTS AND DISCUSSION

Although not presented, results from several preliminary studies served as the basis for the experimental design. Some of the more important findings of these initial studies were that

- The hydrophobic membrane slowed the movement of water vapor as compared to leaving sample vials uncovered, but did not completely prevent this process from occurring,
- No analyte interactions were observed, that is, the same approximate concentration ratios among three different media were obtained regardless if one or more analytes were present,
- Analyte concentrations in all three media were temporal (changed with length of exposure).

The concentrations established for the six analytes studied, in the three different media, appear in Appendix A. There are eight tables in Appendix A, one for each chamber experiment. For both the discrete soil samples and the water samples held in the membrane covered vials, the final weight (weight of moist soil or groundwater) was used to compute the analyte concentrations. The air-dried soils, which started with a moisture content of $<1\%$, ended up with a 2 to 3% moisture content, independent of exposure period length. Samples with initial moisture contents of either 5

and 10% decreased by about one-fourth when held for 22–27 days, and by almost one-half when held from 49 to 55 days. Samples that initially had a 20% moisture content decreased by about 10 and 20% over these two exposure periods, respectively. Likewise between 5 and 15% of the water was also lost from the saturated soil samples. The water samples lost $\leq 5\%$ of their mass over these periods. In addition to the individual water and soil values, the mean, or in one case the single highest value, obtained for the three chamber vapor samples, is reported for each experiment. Extremely low values for the chamber vapor samples were omitted, because they were suspected to have been caused by a needle blockage, thus preventing the proper retrieval or transfer of a gas sample.

The ratio of analyte concentrations between the chamber's vapor and water phases are estimates of the Henry's law constants for these VOCs at 11°C. To determine these ratios, the mean values

for the water sample duplicates was used for each analyte. Table 4 shows the Henry's law constants established for each experiment and the means for each of the six analytes, differentiating between vessels with and without a membrane cover. Also included in Table 4 are some literature values reported by Dewulf et al. (1995) for Henry's law constants for VOCs at 10°C. Overall there was very good agreement between the literature values and mean values determined for the eight chamber experiments. This agreement between experimental and reported Henry's law constants supports the decision to remove the aberrantly low vapor determinations.

The mean values for the two water reservoirs (vessels with and without membrane covers) for seven of the eight experiments were found to be significantly different at the 95% confidence level for both TCE and PCE, using a Student's t-test. A possible explanation for this phenomenon is that the membrane preferentially sorbed chlorinated

Table 4. Estimates of Henry's law constants (vapor/water) for VOCs at 11°C.

<i>Expt.</i>	<i>TDCE</i>	<i>Ben</i>	<i>TCE</i>	<i>Tol</i>	<i>PCE</i>	<i>p-Xyl</i>
1	0.16 0.17n	0.13 0.12n	0.16 0.17n	0.11 0.11n	0.24 0.31n	0.067 0.071n
2	0.14	0.13	0.16	0.11	0.24	0.096
3	0.13 0.14n	0.11 0.11n	0.14 0.16n	0.091 0.10n	0.22 0.29n	0.085 0.093n
4	0.11	0.098	0.13	0.11	0.21	0.12
5	0.15 0.16n	0.11 0.11n	0.15 0.16n	0.11 0.097n	0.22 0.29n	0.088 0.10n
6	0.19 0.21n	0.11 0.11n	0.15 0.16n	0.10 0.11n	0.21 0.27n	0.096 0.10n
7	0.15 0.16n	0.10 0.11n	0.14 0.16n	0.098 0.11n	0.19 0.26n	0.089 0.10n
8	0.18 0.17n	0.11 0.10n	0.14 0.15n	0.098 0.099n	0.19 0.24n	0.087 0.094n
Membrane (8)						
Mean	0.151	0.112	0.146	0.103	0.215	0.0910
s.d.*	0.026	0.012	0.011	0.008	0.019	0.0147
% rsd†	17%	11%	7.5%	7.8%	8.8%	16%
No membrane (6)						
Mean	0.168	0.110	0.160	0.104	0.277	0.0930
s.d.	0.023	0.006	0.006	0.006	0.025	0.0112
% rsd	14%	5.4%	3.8%	7.8%	9.0%	12%
Literature values (Dewulf et al. 1995)						
Mean	—	0.097	0.139	0.106	0.256	0.107
s.d.	—	0.0057	0.0053	0.0091	0.010	0.0080
% rsd	—	5.9%	3.8%	8.6%	4.0%	7.5%

n No membrane (open vessel).

* Standard deviation.

† Percent relative deviation.

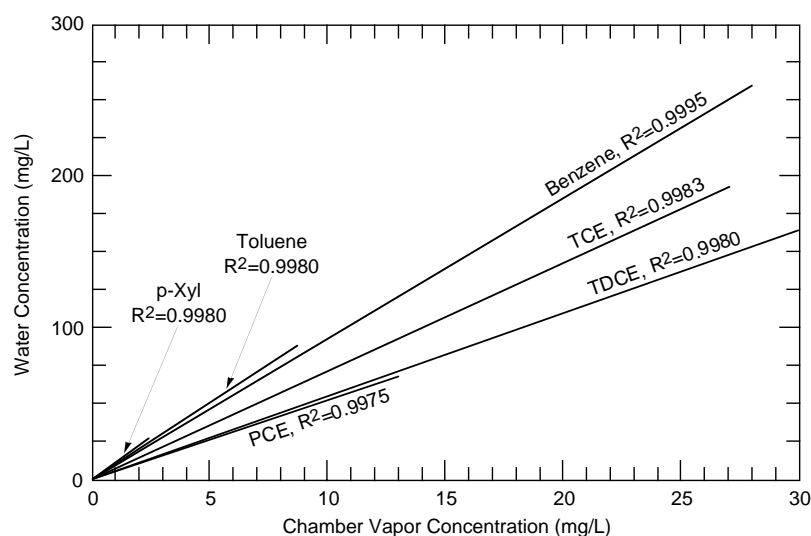


Figure 2. Linear partitioning between chamber vapor and membrane-covered water samples.

compounds, therefore creating a condition where the water inside the membrane covered vials was exposed to an enriched vapor concentration. Aside from this experimental artifact, the relative standard deviation for the mean values was always $\leq 17\%$, and often $< 10\%$. Therefore, consistent with the principles of Henry's law, constant (or linear) partitioning was empirically established over the concentration range tested (Fig. 2).

Duplicate water samples and, in some cases soil samples, were included in the experiment in order to assess the precision of this experimental approach. Overall, the differences among duplicates was small; however, differences among the duplicate water samples were generally smaller than for the soil samples. The discrepancy in precision between these two matrices was probably due to inconsistencies associated with packing a soil into a small vial and losses due to the biological degradation of the aromatic compounds (i.e., Ben, Tol, and p-Xyl).

The amount of water remaining at the end of the exposure period for the three moist soil conditions, and movement of water vapor onto the initially air dried soils, made all of the mineral surfaces hydrated. The presence of moisture and oxygen created conditions conducive to microbiological degradation processes (Atlas 1981). Consistent with these conditions, several very low or nondetectable concentrations for Ben, Tol and p-Xyl were established for soil samples from experiments 1–5 (App. A). Although not anticipated, especially for the CR-D and Wis soils, losses of aromatic hydrocarbons and persistence of chlorinated compounds are consistent with an earlier study (Hewitt 1996). Furthermore, the diminishing of biodegradation losses at high analyte con-

centrations has been observed. Therefore, not only were these five experiments with the lowest analyte concentrations more susceptible to biodegradation, but the rate of biodegradation was greater than the rate of analyte diffusion. Because of the impact of biodegradation on the aromatic hydrocarbon, only the chlorinated compounds were evaluated for the soil samples in experiments 1–5. As with the water samples, the mean of the soil sample duplicates was used for subsequent data interpretations.

Close inspection of the analyte soil concentrations reported in Appendix A shows that the effect of moisture was not always consistent. Two general trends were 1) as the moisture content increased, analyte concentrations decreased for the CR-S soil, and 2) while the CR-D soil showed increasing analyte concentrations with increasing moisture content. There were no trends with regard to moisture in the majority of cases for the Wis soil.

The inconsistencies in trends between soil moisture and analyte concentrations may have been caused by either poor seals between the vial rim and membrane, or inconsistencies in vial packing. To avoid this potential experimental artifact and suppress the influence of moisture altogether, the concept of using a mean value was considered. Before taking this step, the ratio of high to low analyte concentrations for a soil in each experiment was first evaluated. The results of this analysis, with the omission of the saturated condition for the CR-S soil, showed the ratio to be a factor of three or less (75 out of 99 cases, Table 5) for most cases. Therefore the use of mean values could be justified by accepting an uncertainty of a factor three ($\times 3$). Further justification for omitting

Table 5. Ratio (i.e., high:low) of analyte concentration (mg/kg) established for the soil samples. Saturated condition of the CR-S soil is not included.

Expt.	Soil	TDCE	Ben	TCE	Tol	PCE	p-Xyl
1	CR-S	1.6	—	1.4	—	1.5	—
	CR-D	4.2	—	3.0	—	1.9	—
	Wis	4.0	—	1.6	—	2.0	—
2	CR-S	4.9	—	5.3	—	4.7	—
	CR-D	17	—	5.6	—	2.9	—
	Wis	1.9	—	1.7	—	3.1	—
3	CR-S	1.5	—	1.4	—	1.4	—
	CR-D	6.7	—	3.0	—	1.8	—
	Wis	2.6	—	1.2	—	1.2	—
4	CR-S	1.2	—	1.4	—	1.6	—
	CR-D	14	—	4.6	—	2.4	—
	Wis	2.9	—	1.8	—	1.4	—
5	CR-S	1.6	—	1.2	—	1.5	—
	CR-D	6.1	—	4.9	—	2.6	—
	Wis	2.9	—	1.5	—	1.1	—
6	CR-S	1.2	1.7	1.7	2.8	2.2	3.9
	CR-D	3.2	2.8	2.2	1.5	1.5	1.6
	Wis	4.2	1.7	1.5	1.5	1.5	2.7
7	CR-S	1.3	1.4	1.5	2.1	1.9	3.0
	CR-D	3.9	3.0	2.6	1.7	1.9	1.2
	Wis	4.3	2.3	1.8	1.7	1.2	1.8
8	CR-S	1.6	2.2	2.3	3.3	3.0	5.3
	CR-D	4.3	2.4	1.6	1.2	2.2	3.6
	Wis	3.7	2.0	1.6	2.4	4.6	6.9

moisture is that it is not the dominant variable relative to VOC sorption with respect to hydrated soils (Karickhoff et al. 1979, Chiou et al. 1983, Conant et al. 1996). Thus, with the omission of the saturated condition for the CR-S soil, a mean value was used to further evaluate the relationship between chamber analyte vapor and soil concentrations (Table 6).

Among the three soils studied, the unsaturated CR-S soil showed the highest analyte concentrations, while the other two soils had similar, often overlapping analyte concentration ranges (Table 6). The differences between analyte concentrations established for these soils were presumably due to their sorption capacity, of which organic carbon plays an important role (Karickhoff et al. 1979, Chiou et al. 1983). As shown in Table 1, the CR-S soil has the highest organic carbon content.

In theory, soil vapor concentration can be related to bulk soil concentration by the following equation (Rong 1996):

$$C_G = C_T(\rho_b K_H)/[\Theta + (n - \Theta)K_H + \rho_b f_{oc} K_{oc}]$$

where C_G = soil gas concentration in (mg/L)

Table 6. Mean value (mg/kg) and percent standard deviation for analyte concentration established for the soil samples. Saturated condition of the CR-S soil is not included.

Expt.	Soil	TDCE	Ben	TCE	Tol	PCE	p-Xyl	Expt.	Soil	TDCE	Ben	TCE	Tol	PCE	p-Xyl
1	CR-S	0.13 25%	—	0.068 20%	—	0.076 25%	—	5	CR-S	2.3 30%	—	4.4 9.1%	—	5.6 18%	—
	CR-D	0.023 52%	—	0.015 40%	—	0.018 28%	—		CR-D	1.1 75%	—	1.4 56%	—	1.6 35%	—
	Wis	0.020 55%	—	0.019 21%	—	0.028 29%	—		Wis	0.75 67%	—	1.5 19%	—	2.0 2.5%	—
2	CR-S	0.21 105%	—	0.19 79%	—	0.17 100%	—	6	CR-S	24 12%	17 25%	23 30%	19 58%	29 41%	17 76%
	CR-D	0.070 94%	—	0.064 52%	—	0.070 40%	—		CR-D	14 50%	7.6 41%	7.5 32%	4.4 17%	6.9 19%	2.7 18%
	Wis	0.092 35%	—	0.090 21%	—	0.10 41%	—		Wis	10 66%	5.9 22%	8.3 18%	5.4 26%	9.8 16%	4.4 50%
3	CR-S	0.58 21%	—	0.65 15%	—	0.72 22%	—	7	CR-S	12 21%	14 18%	27 22%	22 44%	37 35%	24 58%
	CR-D	0.13 65%	—	0.16 42%	—	0.16 23%	—		CR-D	6.9 64%	6.6 53%	8.6 42%	5.9 29%	10 26%	4.8 8.5%
	Wis	0.12 39%	—	0.22 7.7%	—	0.29 9.7%	—		Wis	5.6 55%	5.8 34%	10 24%	7.1 19%	13 12%	6.8 32%
4	CR-S	4.6 8.3%	—	3.2 21%	—	3.6 26%	—	8	CR-S	98 26%	76 45%	84 52%	62 74%	82 66%	50 94%
	CR-D	1.4 70%	—	0.78 49%	—	0.78 38%	—		CR-D	45 53%	27 37%	21 20%	12 12%	14 29%	8.2 40%
	Wis	1.2 59%	—	1.1 22%	—	1.2 14%	—		Wis	38 56%	28 26%	26 20%	17 47%	22 55%	12 78%

C_T = soil concentration (mg/kg)
 Θ = soil water content by volume (dimensionless)
 n = soil porosity (dimensionless)
 ρ_b = soil density (g/cm³)
 f_{oc} = soil organic carbon content (dimensionless)
 K_H = Henry's law constant (dimensionless)
 K_{oc} = organic carbon partition coefficient (cm³/g).

By letting the conversion coefficient CO equal C_G/C_T ,

$$CO = (\rho_b K_H) / [\Theta + (n - \Theta) K_H + \rho_b f_{oc} K_{oc}].$$

Table 7. Theoretical mean conversion coefficients (CO) between soil vapor concentration (mg/L) and soil matrix concentration (mg/kg) for common VOCs (Rong 1996).

Compound	CO (kg/L)
Vinyl chloride	8.3
Trans-1,2-dichloroethene	1.32
Benzene	1.09
Trichloroethene	1.16
Tetrachloroethene	0.855
Toluene	0.565
o,m,p - Xylene	0.485
1,2-Dichlorobenzene	0.0485

Note: Based on a median soil organic carbon content of 0.14%.

Table 8. Experimental values for conversion coefficient, the ratio of chamber vapor analyte concentration (mg/L) to mean soil concentration (mg/kg).

Expt.	Soil	CO (kg/L)					
		TDCE	Ben	TCE	Tol	PCE	p-Xyl
1	CR-S	0.28	—	0.26	—	0.28	—
	CR-D	1.6	—	1.2	—	1.2	—
	Wis	1.8	—	0.95	—	0.75	—
2	CR-S	0.67	—	0.49	—	0.52	—
	CR-D	2.0	—	1.5	—	1.3	—
	Wis	1.5	—	1.0	—	0.88	—
3	CR-S	0.29	—	0.29	—	0.29	—
	CR-D	1.3	—	1.2	—	1.3	—
	Wis	1.4	—	0.86	—	0.72	—
4	CR-S	0.39	—	0.34	—	0.27	—
	CR-D	1.3	—	1.4	—	1.3	—
	Wis	1.5	—	1.0	—	0.82	—
5	CR-S	0.91	—	0.48	—	0.30	—
	CR-D	1.9	—	1.5	—	1.1	—
	Wis	2.8	—	1.4	—	0.85	—
6	CR-S	1.1	0.54	0.43	0.20	0.28	0.076
	CR-D	1.9	1.2	1.3	0.86	1.2	0.48
	Wis	2.7	1.6	1.2	0.70	0.82	0.30
7	CR-S	1.1	0.56	0.48	0.23	0.27	0.088
	CR-D	1.9	1.2	1.5	0.85	1.0	0.44
	Wis	2.3	1.4	1.3	0.70	0.76	0.31
8	CR-S	0.83	0.37	0.32	0.14	0.16	0.048
	CR-D	1.8	1.0	1.3	0.72	0.93	0.29
	Wis	2.1	1.0	1.0	0.51	0.59	0.20

Means, standard deviations, and relative standard deviations (in parentheses)

CR-S	0.696	0.490	0.386	0.190	0.296	0.0707
	±0.343	±0.104	±0.094	±0.046	±0.100	±0.0205
	(49%)	(21%)	(24%)	(24%)	(34%)	(29%)
CR-D	1.71	1.13	1.36	0.810	1.17	0.403
	±0.28	±0.12	±0.13	±0.078	±0.14	±0.100
	(16%)	(11%)	(9.6%)	(9.6%)	(12%)	(25%)
Wis	2.01	1.33	1.09	0.637	0.774	0.273
	±0.55	±0.31	±0.19	±0.110	±0.092	±0.055
	(27%)	(23%)	(17%)	(17%)	(12%)	(20%)

Average CO values can be determined based on the mean or median, in the case of a lognormal distribution, physical properties of soils and reported K_H and K_{OC} values for organic compounds. When Rong (1996) performed this analysis for 55 soils with a median organic carbon content of 0.14%, the CO values listed in Table 7 were obtained. His study, which involved several more VOCs than listed in Table 7, predicted that extremely volatile compounds with high Henry's law constants would have high CO values. Conversely, compounds with extremely low volatility and low Henry's law constants would have low CO values. Furthermore, that the most frequently occurring soil contaminants, i.e., TCE, PCE and Ben (Plumb and Pitchford 1985), would have CO values of around one.

Experimental estimates for CO can be calculated using the mean bulk soil concentrations in Table 6 (unsaturated CR-S soil values only) and the chamber vapor concentrations listed in Appendix A. These experimental CO values (see Table 8), although sometimes not as precise as the Henry's law constants shown in Table 4, also resulted in fairly constant ratios (linear partitioning) suggesting that proportional constants exist between these two media (Fig. 3). With regard to soil type, the mean ratio for the unsaturated CR-S soil was always significantly different at the 95% confidence level from the other two soils, while the CR-D and Wis soil were only significantly different from each other for two of the six analytes tested. The lower ratios for the CR-S soil were due to its higher analyte sorption capacity, i.e., organic carbon content. More importantly, ratios for the two low organic carbon (<0.2%) soils in Table 8 show values that are close to unity for Ben, TCE, and PCE. Furthermore, the higher ratio obtained for TDCE and conversely the lower one for

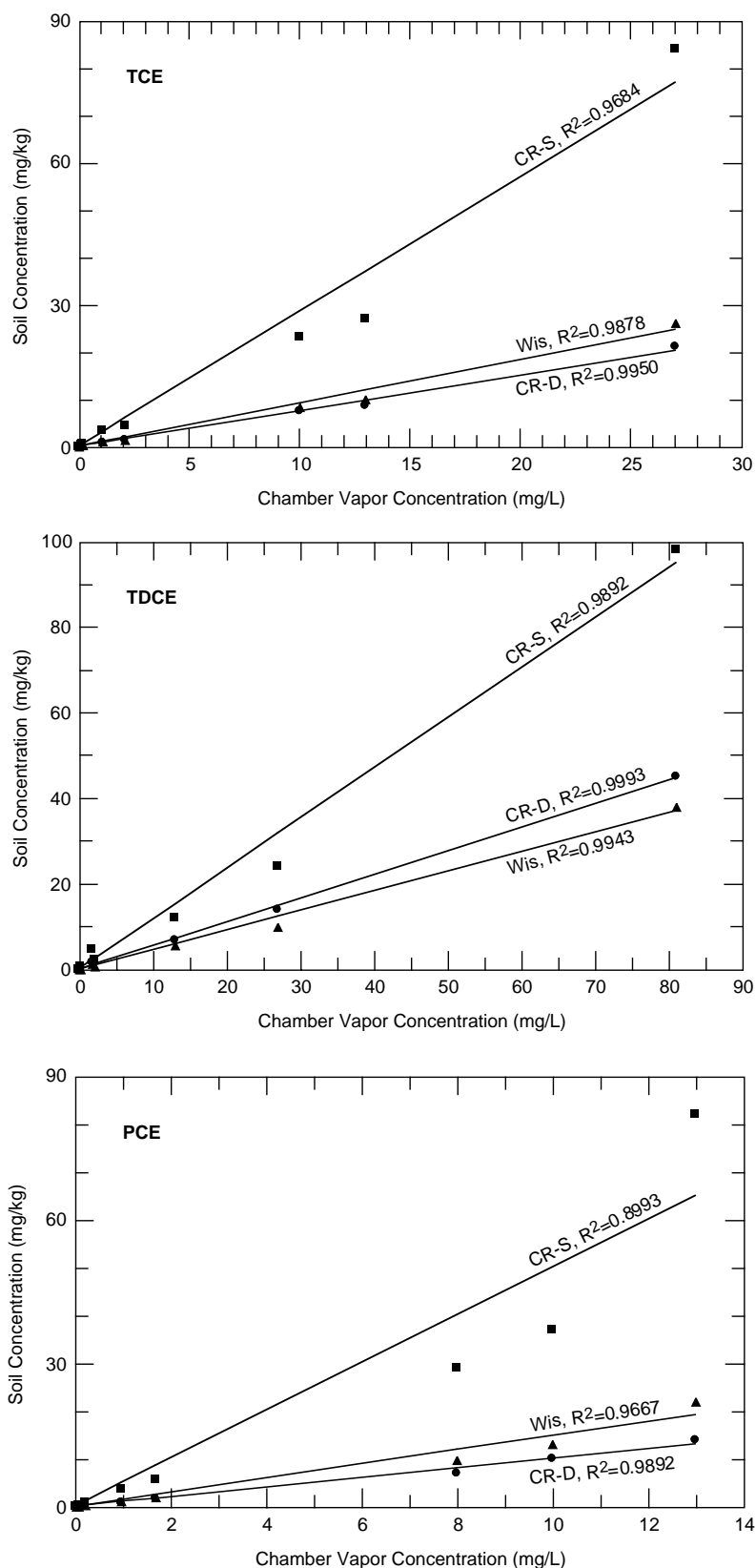


Figure 3. Linear partitioning between chamber vapor and soil samples for the chlorinated analytes.

p-Xyl are also consistent with the trends established by the theoretical analysis of Rong (1996).

These laboratory findings support the assumption that linear partitioning exists between soil vapor and bulk soil VOC concentrations as inferred by Conant et al. (1996) and Rong (1996). Furthermore, that the sorption of VOCs by soil under conditions where mineral surfaces are hydrated (but perhaps unsaturated with respect to bulk water content) is likely to be more dependent on the organic carbon content than moisture content.

To further substantiate the concept that linear partitioning exists between soil vapor and bulk soil VOC concentrations, a field study should be performed. Because of the potential problems cited previously, special attention should be given to both the collection of soil vapor and soil samples. Small volume soil gas probes (Conant et al. 1996) and a soil coring device that collects and transfers a sample with limited disruption and exposure (Hewitt 1996) would complement this effort. In addition, a site that has VOC concentrations ranging over several orders of magnitude in the near-surface unsaturated zone should be selected. The reason for initially attempting to establish this relationship with near-surface soils is that collecting soil from depths greater than several meters is difficult without inducing volatilization losses using conventional downhole procedures (Hewitt 1996, Hewitt and Lukash 1996).

Establishing a linear relationship between vapor concentrations and soil concentrations could have a profound effect on future site characterization activities. The development of a soil gas measurement procedure that would allow computation of soil concentrations to within an order of magnitude of the actual concentration would expedite site characterization and significantly reduce the cost of site characterization. Soil gas probes can be rapidly installed and sampled, which coupled with on-site analysis techniques, allows for near-real-time vertical and horizontal profiling. Furthermore, because most subsurface soils generally have low organic carbon contents (<0.20%), CO values may have a broad range of applications with regard to soil type.

SUMMARY

The findings of this laboratory experiment provide preliminary support for the theory that linear partitioning exists between soil vapor and

bulk soil VOC concentrations under environmental conditions. Additionally, these findings support the view that the organic carbon content is the dominant variable controlling the capacity of a soil to retain VOCs.

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APPENDIX A: CHAMBER EXPERIMENTS

Concentrations Established for Soil, Water, and Vapor Samples

Experiment 1. Measured concentrations for chamber study using a 0.1- μ L volume of VOCs in 5 mL of tetraglyme fortification solution and a 26-day exposure period.

Sample	TDCE	Ben	TCE	Tol	PCE	p-Xyl
CRREL surface (mg/kg)						
Dry	0.14	0.004	0.075	0.020	0.097	0.035
10%	0.16	0.0004	0.084	0.004	0.087	ND*
20%	0.097	0.0002	0.062	0.0002	0.065	ND
Sat'd	0.083	0.0001	0.053	ND	0.056	ND
CRREL deep (mg/kg)						
Dry	0.008	0.0003	0.007	0.001	0.011	0.003
10%	0.018	0.0001	0.013	ND	0.021	ND
20%	0.031	0.0002	0.018	ND	0.020	ND
Sat'd	0.034	0.0002	0.021	ND	0.021	ND
Wisconsin (mg/kg)						
Dry	0.008	0.0004	0.014	0.004	0.026	0.008
5%	0.016	0.0004	0.020	0.0006	0.036	0.001
10%	0.026	0.0001	0.023	0.0001	0.034	0.009
Sat'd	0.032	ND	0.018	ND	0.018	ND
Water—membrane (mg/L)						
1	0.21	0.007	0.11	0.018	0.083	0.015
2.	0.23	0.007	0.12	0.018	0.090	IF [†]
Water—no cover (mg/L)						
1	0.20	0.007	0.10	0.016	0.063	0.014
2	0.22	0.008	0.11	0.019	0.071	0.014
Chamber gas (mg/L)						
	0.036	0.0009	0.018	0.002	0.021	0.001

* Not detected.

† Instrumental failure.

Experiment 2. Measured concentrations for chamber study using a 1.0- μ L volume of VOCs in 5 mL of tetraglyme fortification solution and a 22-day exposure period.

Sample	TDCE	Ben	TCE	Tol	PCE	p-Xyl
CRREL surface (mg/kg)						
Dry 1	0.47	0.056	0.36	0.22	0.40	0.24
Dry 2	0.56	0.057	0.36	0.23	0.40	0.24
10% 1	0.12	0.002	0.077	0.017	0.10	0.033
10% 2	0.27	0.002	0.23	0.070	0.28	0.11
20% 1	0.091	0.001	0.069	0.002	0.092	0.006
20% 2	0.12	ND*	0.068	0.0006	0.080	ND
Sat'd	0.034	0.001	0.028	0.0008	0.020	ND
CRREL deep (mg/kg)						
Dry 1	0.011	0.003	0.018	0.012	0.034	0.022
Dry 2	0.0064	0.002	0.015	0.012	0.035	0.024
10% 1	0.050	0.006	0.060	0.011	0.10	0.007
10% 2	0.075	0.011	0.075	0.026	0.099	0.022
20% 1	0.14	0.012	0.093	0.017	0.088	0.009
20% 2	0.15	0.016	0.093	0.021	0.076	0.012
Sat'd	0.13	0.009	0.078	0.001	0.063	ND
Wisconsin (mg/kg)						
Dry	0.064	0.013	0.099	0.050	0.12	0.066
5%	0.066	0.011	0.086	0.032	0.12	0.042
10%	0.12	0.014	0.11	0.012	0.13	0.025
Sat'd	0.12	0.005	0.066	0.009	0.042	0.013
Water—membrane (mg/L)						
1	1.1	0.14	0.63	0.25	0.38	0.14
2.	0.95	0.13	0.56	0.23	0.36	0.13
Chamber gas (mg/L)						
	0.14	0.018	0.094	0.026	0.088	0.013

* Not detected

Experiment 3. Measured concentrations for chamber study using a 1.0- μ L volume of VOCs in 5 mL of tetraglyme fortification solution and a 55-day exposure period.

<i>Sample</i>	<i>TDCE</i>	<i>Ben</i>	<i>TCE</i>	<i>Tol</i>	<i>PCE</i>	<i>p-Xyl</i>
CRREL surface (mg/kg)						
Dry	0.55	0.018	0.75	0.30	0.91	0.56
10%	0.48	0.002	0.55	0.14	0.63	0.25
20%	0.71	0.001	0.66	ND*	0.63	ND
Sat'd	0.25	ND	0.28	ND	0.27	ND
CRREL deep (mg/kg)						
Dry	0.030	0.001	0.071	0.027	0.12	0.061
10%	0.088	0.003	0.13	0.034	0.21	0.048
20%	0.20	0.0008	0.21	ND	0.16	ND
Sat'd	0.20	0.002	0.21	0.004	0.16	ND
Wisconsin (mg/kg)						
Dry	0.069	0.004	0.19	0.071	0.28	0.15
5%	0.11	0.005	0.22	0.070	0.31	0.14
10%	0.14	ND	0.22	ND	0.31	ND
Sat'd	0.18	ND	0.23	ND	0.25	ND
Water—membrane (mg/L)						
1	1.3	0.046	1.4	0.37	0.94	0.36
2.	1.3	0.044	1.3	0.38	0.96	0.30
Water—no cover (mg/L)						
1	1.2	0.046	1.2	0.34	0.74	0.31
2	1.2	0.044	1.2	0.34	0.72	0.29
Chamber gas (mg/L)						
	0.17	0.005	0.19	0.034	0.21	0.028

* Not detected.

Experiment 4. Measured concentrations for chamber study using a 10- μ L volume of VOCs in 5 mL of tetraglyme fortification solution and a 22-day exposure period.

<i>Sample</i>	<i>TDCE</i>	<i>Ben</i>	<i>TCE</i>	<i>Tol</i>	<i>PCE</i>	<i>p-Xyl</i>
CRREL surface (mg/kg)						
Dry 1	4.9	2.3	4.4	3.5	5.1	3.6
Dry 2	4.8	1.9	3.6	3.0	4.1	3.2
10% 1	4.9	0.91	2.9	1.7	3.4	1.5
10% 2	3.4	1.2	IF*	1.8	3.2	1.6
20% 1	5.2	0.35	2.9	0.97	2.9	0.53
20% 2	4.6	0.91	2.7	1.4	2.7	1.1
Sat'd	0.73	0.60	0.49	0.059	0.33	0.33
CRREL deep (mg/kg)						
Dry 1	0.14	0.012	0.22	0.25	0.46	0.35
Dry 2	0.18	0.015	0.26	0.25	0.46	0.31
10% 1	1.4	0.057	0.84	0.45	0.98	0.33
10% 2	0.81	0.047	0.75	0.47	1.2	0.42
20% 1	2.1	0.090	1.1	0.58	0.98	0.32
20% 2	2.2	0.095	1.1	0.59	0.90	0.32
Sat'd	2.2	0.048	1.0	0.30	0.60	0.14
Wisconsin (mg/kg)						
Dry	0.72	0.058	1.1	0.90	1.4	0.98
5%	0.5.2	0.036	0.73	0.43	1.0	0.28
10%	1.3	0.054	1.1	0.52	1.2	0.30
Sat'd	2.1	0.001	1.3	0.002	1.3	0.057
Water—membrane (mg/L)						
1	18	7.3	8.6	4.1	4.5	1.7
2	16	7.0	8.4	4.2	4.8	1.7
Chamber gas (mg/L)						
	1.8	0.70	1.1	0.46	0.98	0.20

* Instrument failure.

Experiment 5. Measured concentrations for chamber study using a 10- μ L volume of VOCs in 5 mL of tetraglyme fortification solution and a 50-day exposure period.

<i>Sample</i>	<i>TDCE</i>	<i>Ben</i>	<i>TCE</i>	<i>Tol</i>	<i>PCE</i>	<i>p-Xyl</i>
CRREL surface (mg/kg)						
Dry 1	2.5	1.6	5.6	4.1	7.0	5.5
Dry 2	1.6	1.1	4.1	3.7	6.4	5.3
10% 1	2.1	1.1	4.3	2.9	5.7	3.5
10% 2	1.7	0.94	3.7	2.6	5.3	3.3
20% 1	3.3	1.1	4.3	2.2	4.5	1.6
20% 2	2.9	1.1	4.3	2.2	4.6	1.9
Sat'd	1.0	0.80	1.2	0.067	0.86	0.153
CRREL deep (mg/kg)						
Dry 1	0.31	0.20	0.59	0.42	0.84	0.52
Dry 2	RI	0.093	0.37	0.35	0.67	0.49
10% 1	0.61	0.37	1.1	0.61	1.7	0.65
10% 2	0.49	0.34	0.98	0.63	1.8	0.81
20% 1	1.7	0.80	1.7	0.82	1.5	0.46
20% 2	1.8	0.90	2.2	1.1	2.5	0.83
Sat'd	1.9	0.82	2.1	0.94	1.7	0.50
Wisconsin (mg/kg)						
Dry	0.53	0.44	1.4	1.0	2.0	1.2
5%	0.52	0.42	1.4	0.91	2.0	1.1
10%	0.45	0.34	1.3	0.78	2.0	0.90
Sat'd	1.5	0.022	2.0	0.48	1.9	0.65
Water—membrane (mg/L)						
1	14	6.9	14	6.5	7.8	3.3
2	14	6.5	14	5.9	7.5	3.3
Water—no cover (mg/L)						
1	14	6.9	14	6.9	6.2	3.0
2	13	6.8	12	6.7	5.6	2.8
Chamber gas (mg/L)						
	2.1	0.75	2.1	0.66	1.7	0.29

Experiment 6. Measured concentrations for chamber study using a 100- μ L volume of VOCs in 4.5 mL of tetraglyme fortification solution and a 24-day exposure period.

<i>Sample</i>	<i>TDCE</i>	<i>Ben</i>	<i>TCE</i>	<i>Tol</i>	<i>PCE</i>	<i>p-Xyl</i>
CRREL surface (mg/kg)						
Dry 1	21	21	30	32	43	33
Dry 2	24	24	32	32	42	31
10% 1	24	14	20	13	24	9.9
10% 2	20	13	20	13	24	10
20% 1	25	13	17	11	18	7.5
20% 2	29	16	20	12	21	8.8
Sat'd	36	17	18	10	13	4.7
CRREL deep (mg/kg)						
Dry 1	7.1	4.1	4.6	3.7	5.5	3.4
Dry 2	5.3	3.5	4.1	3.4	5.1	3.2
10% 1	8.7	5.4	5.9	3.5	6.7	2.2
10% 2	12	6.9	7.6	4.6	9.7	3.3
20% 1	20	10	9.5	5.1	6.9	2.4
20% 2	20	11	9.9	5.4	8.5	2.8
Sat'd	20	9.8	9.1	4.7	6.4	2.1
Wisconsin (mg/kg)						
Dry	4.5	5.5	7.8	7.4	12	7.6
5%	5.9	4.6	6.5	4.3	9.1	3.6
10%	12	7.6	8.8	5.2	10	3.7
Sat'd	19	5.8	10	4.8	8.1	2.8
Water—membrane (mg/L)						
1	150	86	72	38	41	14
2	130	76	65	35	36	13
Water—no cover (mg/kg)						
1	150	87	65	37	30	13
2	140	80	62	33	29	12
Chamber gas (mg/L)						
	27	9.2	10	3.8	8.0	1.3

Experiment 7. Measured concentrations for chamber study using a 100- μ L volume of VOCs in 5 mL of tetraglyme fortification solution and a 49-day exposure period.

<i>Sample</i>	<i>TDCE</i>	<i>Ben</i>	<i>TCE</i>	<i>Tol</i>	<i>PCE</i>	<i>p-Xyl</i>
CRREL surface (mg/kg)						
Dry 1	7.8	15	31	32	49	39
Dry 2	12	18	36	34	55	41
10% 1	11	12	24	18	34	18
10% 2	10	11	22	17	31	17
20% 1	15	14	24	15	27	13
20% 2	14	14	23	16	28	14
Sat'd	11	9.0	8.7	5.0	5.0	1.8
CRREL deep (mg/kg)						
Dry 1	3.4	3.5	5.3	4.5	6.5	5.1
Dry 2	2.3	2.9	4.7	4.2	6.3	4.8
10% 1	3.0	3.7	6.3	4.3	9.6	4.1
10% 2	3.6	4.2	6.8	4.7	10	4.4
20% 1	11	9.6	12	7.1	12	4.9
20% 2	10	9.4	12	7.4	12	5.3
Sat'd	11	9.7	13	7.5	12	5.1
Wisconsin (mg/kg)						
Dry	5.4	6.5	11	9.4	15	10
5%	2.3	3.6	7.3	5.4	12	5.5
10%	4.8	5.1	9.4	6.1	14	6.0
Sat'd	9.8	8.2	13	7.5	12	5.5
Water—membrane (mg/L)						
1	87	78	93	50	52	24
2	84	75	89	52	52	23
Water—no cover (mg/L)						
1	86	78	88	51	42	23
2	75	70	73	44	36	19
Chamber gas (mg/L)						
	13	7.9	13	5.0	10	2.1

Experiment 8. Measured concentrations for chamber study using a 500- μ L volume of VOCs in 2.0 mL of tetraglyme fortification solution and a 25-day exposure period.

<i>Sample</i>	<i>TDCE</i>	<i>Ben</i>	<i>TCE</i>	<i>Tol</i>	<i>PCE</i>	<i>p-Xyl</i>
CRREL surface (mg/kg)						
Dry 1	130	110	130	110	140	96
Dry 2	120	120	140	120	150	110
10% 1	79	52	56	35	50	23
10% 2	73	53	59	38	56	27
20% 1	96	60	59	35	50	22
20% 2	90	60	60	34	48	21
Sat'd	68	41	24	11	7.6	2.8
CRREL deep (mg/kg)						
Dry 1	17	16	16	14	15	12
Dry 2	13	14	15	13	15	12
10% 1	34	23	20	12	18	7.3
10% 2	41	23	20	10	16	5.9
20% 1	64	37	26	14	16	6.4
20% 2	62	35	25	13	13	5.3
Sat'd	65	35	23	11	7.7	3.3
Wisconsin (mg/kg)						
Dry	22	27	33	29	38	25
5%	18	18	21	13	22	9.1
10%	46	29	26	14	20	8.4
Sat'd	66	36	24	12	8.2	3.6
Water—membrane (mg/L)						
1	410	250	200	87	67	27
2	480	270	190	91	71	28
Water—no cover (mg/L)						
1	460	270	170	85	53	25
2	480	280	180	90	53	27
Chamber gas (mg/L)						
	81	28	27	8.7	13	2.4

REPORT DOCUMENTATION PAGE

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